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14. ABSTRACT A supported silver adsorbent (Ag/TiO ₂) for sulfur removal from liquid fuels has been developed and characterized. The adsorbent's formulation, preparation procedure, desulfurization conditions and regeneration procedure have established and optimized. In a comparative study, this adsorbent and several other promising adsorbents such as Cu-Y and Ag/Al ₂ O ₃ and PdCl ₂ /Al ₂ O ₃ have been tested and evaluated with model fuels and logistic fuel (i.e. JP-5). It is found that Ag/TiO ₂ demonstrated a high saturation capacity of 15 mg of sulfur/g of adsorbent, and that no special regeneration media or reactivation procedures are required for its regeneration. This high-performance adsorbent enables novel process design for the logistic fuel desulfurization.					
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Final Report
for
**High Contacting Efficiency Carrier Structures & Processes for Liquid Phase
Regenerable Desulfurization of Logistic Fuels**
Contract number: N00014-06-1-1165

Oxygen chemisorption

The activity of the Ag/TiO₂ composition is affected by the procedure for preparation. Conditions during the impregnation, drying and calcination steps play a significant role in the desulfurization effectiveness of the resulting adsorbent. Certain batches were observed to have varied affinities for different sulfur groups present in JP5. Variation in capacities for total sulfur was also observed.

The observed variation in performance is a result of the variation in morphology of the active species (Ag/AgO) on the support surface. Thus a study of the distribution of Ag on the surface of TiO₂ and the effect on desulfurization performance would enable the development of a correlation between preparation procedures, desulfurization performance and surface morphology. Such a study may be warranted if the high atomic Ag utilization (98% reported earlier on 2.0Wt. %Ag/TiO₂) in the case of a real fuel as JP5 can be achieved at higher Ag loadings. This will point out the conditions conducive to higher sulfur capacities. Static volumetric chemisorption was carried out on the Qunatachrome Autosorb AS-1 apparatus shown in Figure 1. In this method, the pressure of a known volume of gas is measured; then the gas is expanded into an evacuated known volume that included the sorbent, and the pressure is measured again. Several pressure measurements are made with progressively higher pressures. This uptake data is referred to as the isotherm.

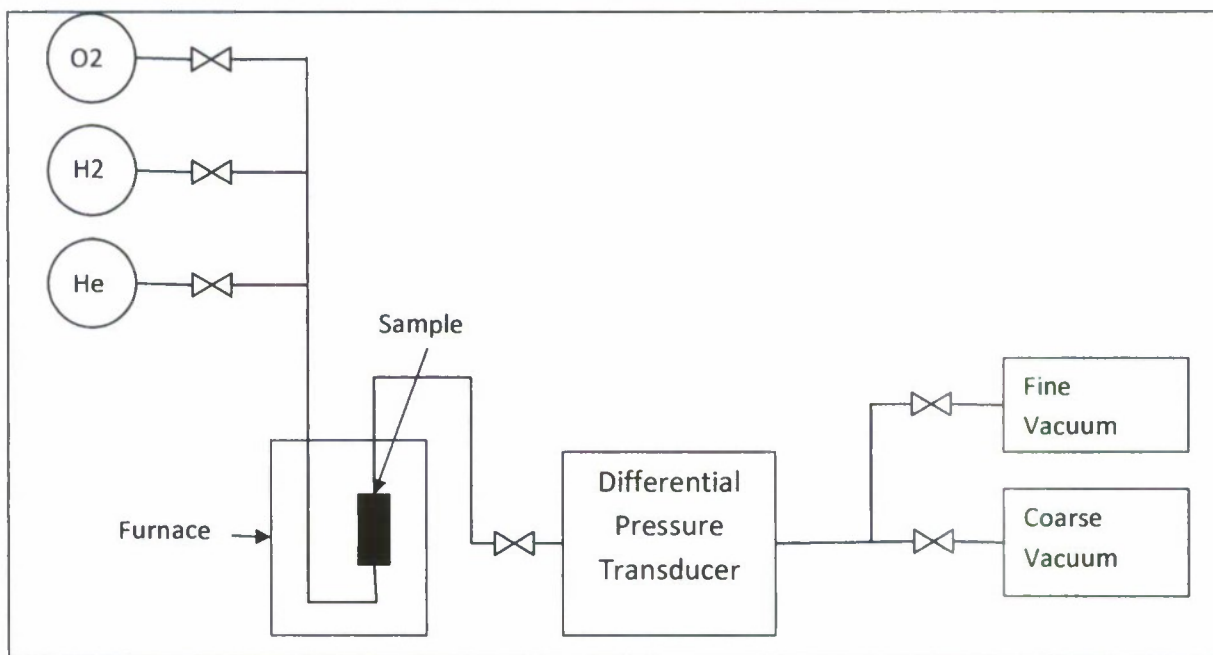


Figure 1. The Quantachrome AS-1 static volumetric chemisorption apparatus

Among the various gases used as an adsorbate, oxygen has been used successfully for Ag catalysts. Two kinds of interactions occur between the Ag atoms and the gas. A weak interaction is referred to as physisorption and the stronger as chemisorption differentiated by the heat of adsorption between the two cases. This difference in behavior is utilized in determining the number of Ag atoms exposed to the surface of the gas from atoms in the bulk of the metal. The technique can thus give information of the dispersion of the active material on the surface of a support such as TiO₂.

The measurements are sensitive to whether the adsorbing gas forms a monolayer on the Ag surface, whether there is a spill-over of the O₂ atoms to the TiO₂ surface and the diffusion of O₂ into the bulk of the Ag crystallite. Several researchers have determined that at 170C these conditions are minimized[1, 2]. The technique is also sensitive to the pre-treatment of the Ag surface prior to chemisorption test. The pretreatment conditions followed are listed in Table 1. Conditions providing the most accurate results have been reported in the literature. These procedures were adapted for use in Ag/TiO₂[2-6].

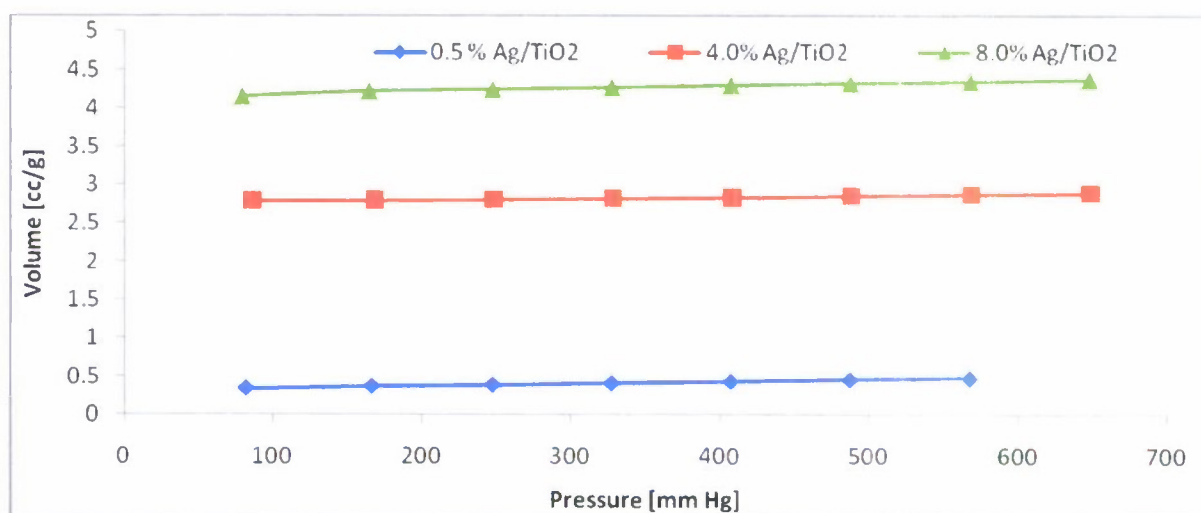


Figure2 Oxygen chemisorption on Ag supported on TiO₂

Oxygen isotherms for the Ag/TiO₂ system are shown in Figure 2. The isotherms represent the combined strong and weak (chemisorption and physisorption) of O₂ on the Ag. From literature the weakly bound O₂ on Ag is minimal compared to the strongly bound. Thus the combined O₂ uptake can be considered to represent the strongly bound oxygen. The adsorption uptakes were determined by extrapolating the isotherm back to zero pressure.

Surface Preparation/removal of organics	Evacuate for 15 min
Reduce oxides to Ag metal	Heat catalyst sample to 300C at 10C/min in H ₂
	Hold at 300C for 60 min*
Remove adsorbed hydrogen	Evacuate for 60min at 300C
Isotherm measurements	Cool to 170C while evacuating system
	Switch gas to O ₂
	Stabilize and obtain isotherms at 170C

Table 1. Reported pretreatment of Ag adsorbent for chemisorption [2]*reported was 180min

The Ag/TiO₂ adsorbents were prepared as follows. The TiO₂ support was dried for 8h at 110C. The support was impregnated with the required concentration of AgNO₃ as per the Wt. loadings. The support was exposed to water saturated air for a period of 2h prior to impregnation. The impregnation volume was 95% of the pore volume of the TiO₂ support. The samples were dried in a vacuum of approximately 50m Torr for 2h followed by calcination at 400C for 2h. For consistency all batches were 15g.

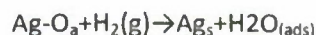
The data obtained on the morphology of the Ag/TiO₂ are listed in Table 2. It may be observed that the higher dispersions were indicated by these studies compared to studies reported earlier (Nov. 2007). The differences are due to the pretreatment conditions used in both the cases. Earlier a reduction temperature of 100C was used which was insufficient to reduce the entire surface Ag to the metallic state. This resulted in lower O₂ uptake during the isotherm measurement and higher crystallite sizes. Lower reduction temperatures were chosen to prevent the sintering of the Ag crystallites to larger sizes. However the effect of sintering was found to be minimal by previous research[1].

Composition[% Wt. Ag]	Saturation sulfur capacity [mgS/g]	Active metal surface area[m ² /g]	Dispersion[%]	Avg. crystallite size[A]	Monolayer uptake [umol/g]	Correlation coefficient
0.5	2.556	0.7611	31.35	37.54	14.53	0.9992
4.0	3.100	6.489	33.41	35.22	123.9	0.9882
8.0	2.754	9.693	24.96	47.16	185.1	0.9885
Data from literature[5]						
1.86	-	-	46.00	29.0	42.0	-

Table 2. Chemisorption data obtained for Ag/TiO₂ adsorbent obtained from the static volumetric chemisorption and comparison with data from literature

Oxygen hydrogen titration

Hydrogen reacts stoichiometrically with adsorbed oxygen layer on Ag surfaces at 170C as described by the reaction:



This stiochiometric reaction between hydrogen and surface oxygen provides the following advantages for characterizing Ag adosrbents/catalysts:

1. Rapid equilibration
2. Increased sensitivity
3. No oxygen contamination effects
4. Distinguishes any irreversible oxygen uptake on the support from that on Ag

A preliminary oxygen-hydrogen titration run was carried out on the Quantachrome instrument on the Ag/TiO₂ adsorbent to corroborate the data obtained from the oxygen chemisorption described in the previous section. H₂ gas is used to titrate the O₂ on the silver surface. For this purpose, the system is

evacuated for 20 minutes after obtaining the oxygen isotherm and then H₂ is dosed into the system and resulting pressures after equilibration is measured. The isotherms were obtained at 170C, shown in Figure 3. The water formed as a result of the titration is absorbed by the TiO₂ support.

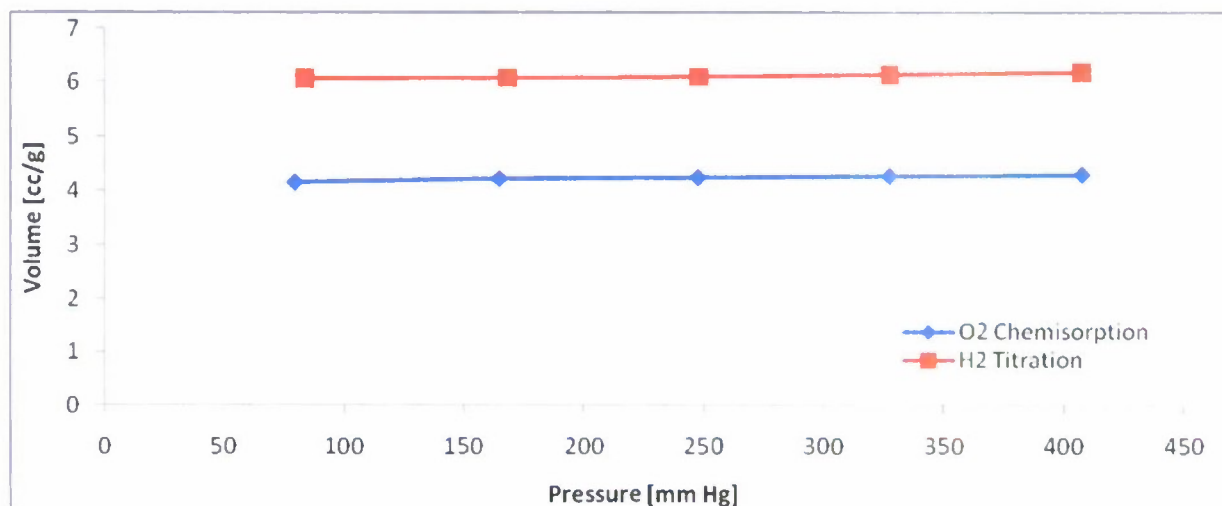


Figure 3. Isotherms representing hydrogen titration of chemisorbed oxygen

	Sample	Monolayer uptake[umol/g]	H2 titr/O2 strong	% Metal dispersion	Avg. crystallite size[A]
Oxygen chemisorption	8.0 Wt. % Ag-TiO ₂	185.1	1.33	24.90	47.16
Hydrogen titration	8.0 Wt. % Ag - TiO ₂	247.1		33.33	35.31

Table 3. Comparison of oxygen chemisorption with oxygen-hydrogen titration

A comparison of the measurements between oxygen chemisorption and hydrogen titration are listed in Table 3. The ratio of the H₂ titrated to the chemisorbed O₂ was observed to be 1.33. The reported value is close to 2. The difference between the observed data and reported uptakes maybe either due to reversible chemisorption on the support or due to reversible adsorption of H₂ on the Ag surface. Both these quantities can be quantified from re-adsorption measurements. This needs to be carried out in further studies.

Batch Equilibration tests

It has been observed that the Ag/TiO₂ adsorbent composition gave consistently lower capacity during a saturation test compared to a dynamic break-through test. Saturation tests are carried out by treating a specific amount of adsorbent with a known weight of JP5/model fuel and mechanically agitating the solution for 48h. The sulfur content of the resulting fuel is analyzed to determine the total sulfur capacity.

The difference in capacity maybe due to equilibrium between the sulfur in the fuel and that attached to the adsorbent. It could also be due to a selectivity issue where in only certain compounds are only removed by the adsorbent. Thus at saturation these compounds are not removed. However the breakthrough occurs due to the displacement of certain sulfur species from the surface by other species adhering to the surface. Thus the total sulfur capacity of the adsorbent during a breakthrough test is possibly due to the continuous capture of a large group of sulfur compounds displacing a smaller group of sulfur compounds.

Thus the saturation sulfur capacity of an adsorbent obtained through an equilibrium test cannot be compared to the saturation capacity obtained from a breakthrough test. Thus batches of Ag/TiO₂ prepared were compared in capacity by batch equilibration tests. Several new compositions were tested for saturation sulfur capacity.

- a) **Multiple impregnations:** The higher Ag utilization has not been observed for adsorbents where there was a higher loadings of silver beyond 2.0 Wt. %. This is due to the formation of larger silver crystallites when using a higher concentration impregnation solution as confirmed by the chemisorption studies. The samples were impregnated a second time using the same concentration solution after drying and calcination following the first impregnation cycle. Thus it is assumed that the Ag crystallites formed during the first impregnation cycle are anchored on the TiO₂ surface before the second impregnation. Thus new crystallites can be formed on the surface during the second impregnation cycle. However, if the existing silver crystallites from the first cycle act as nucleation sites during the second cycle, this will only result in the formation of bigger Ag crystals. This can be confirmed through chemisorption studies.
- b) **Spontaneous monolayer dispersion:** This technique has been described by previous researchers as a method to deposit a consistent layer of a metal halide or acetate on a support[7-9]. Silver chloride has not been shown to display this property previously. An attempt was made to disperse silver chloride as a monolayer on the TiO₂ surface. The TiO₂ support was mixed with AgCl in a ratio 2:1. The mixture was loaded in a quartz reactor and purged with He gas and then heated to the dispersion temperature of 227.5C for 24h. The resulting composition was tested for desulfurization performance with JP5.
- c) **Dispersed cesium on TiO₂ surface:** A monolayer of Cs on a support has been demonstrated to reduce the crystallite size of Ag in catalysts [10]. Cs was deposited on the TiO₂ surface prior to the deposition of Ag. CsNO₃ with a concentration (reported in literature) of approximately 4ppmw was used for the incipient wetness method. The resulting composition was dried at 110C for 8h and then calcined at 400C for 3h. After cooling down to room temperature was impregnated with AgNO₃. The resulting composition was then vacuum dried and calcined following the usual procedure.
- d) **TiO₂ Support:** TiO₂ support with different surface morphology (Type 2) was obtained from Saint Gobain. The characteristic properties of the new material in comparison to the previous are listed in the following table. The preparation procedure was similar to that followed for the type 1 support: wetness impregnation to 95% of the pore volume, vacuum drying and calcination at 400C for 2h.

Type	Surface area [m ² /g]	Avg. pore volume [cc/g]	Median pore diameter [Å]
1	153	0.46	158
2	124	0.57	325

- e) Ag loading: To provide a comparison basis for the saturation equilibrium sulfur capacity for the previous tests batches with varying Ag loading was also prepared. Also tested was PdCl₂ monolayer dispersed on activated alumina as a comparison basis.

The desulfurization performances of these different compositions are shown in Figure 4.

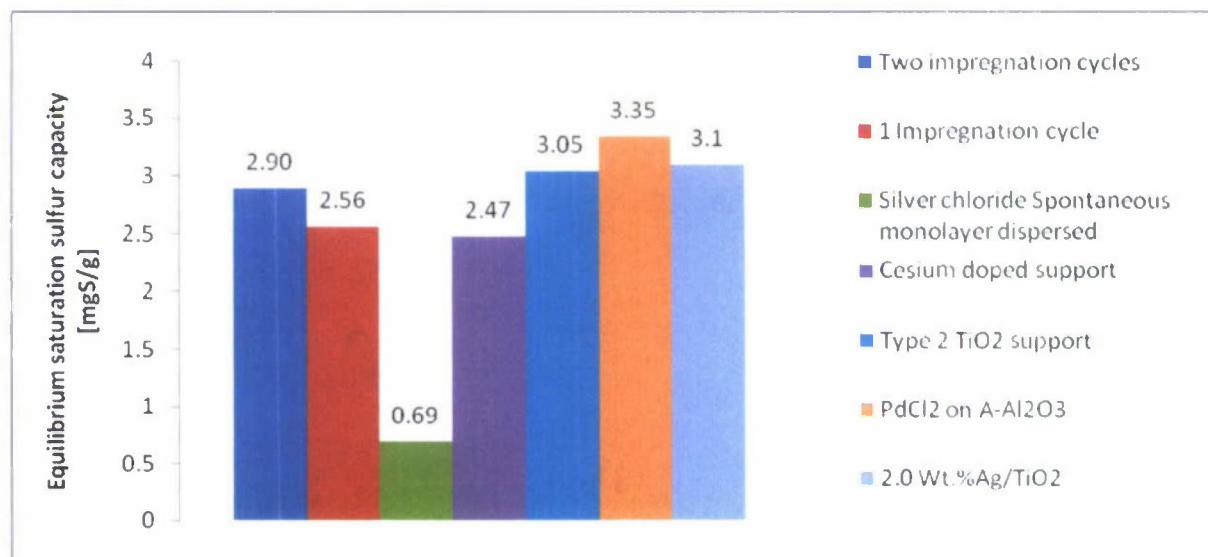


Figure 4. Equilibrium total sulfur capacities of compositions tested

As a basis point for comparison, the capacity for the Ag/TiO₂ is 3.10mgS/g. PdCl₂ supported on Activated alumina showed the highest sulfur capacity among the compositions tested at 3.35mgS/g in comparison. The sulfur capacity increased only by 13% after the second impregnation. Thus the extra Ag atoms added did not provide a significant improvement in capacity. This might be due to the effect of nucleation sites as mentioned earlier. The difference in morphology between the two cases can be observed by static chemisorption techniques. Multiple impregnations may not be the right technique to increase the Ag loading without sacrificing atomic Ag utilization. Doping of the surface with Cs did not enhance the sulfur capacity of the composition. Type 2 TiO₂ showed good capacity at 3.05 mgS/g.

Further improvements may be achieved by pre-treatment of the TiO₂ surface prior to the deposition of silver. The composition of the impregnation solution may also be altered to provide a different interaction with the TiO₂ surface so as to provide better dispersion of silver/smaller crystallites. The reason for low equilibrium saturation sulfur capacity compared to capacity observed during breakthrough tests needs to be explained. Further equilibrium tests with model fuels will help in providing mechanistic information which will explain the behavior with real fuels.

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